

Dehydration of Isopropyl Alcohol on Lithium Vanadium Bronzes —The Relation Between Electrical and Catalytic Properties

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The catalytic decomposition of isopropyl alcohol (IPA) on V_2O_5 and lithium doped V_2O_5 has been studied. The reaction is predominantly dehydration with very little dehydrogenation of IPA. An increase in the concentration of lithium increases the electrical conductivity (σ) and also catalytic dehydration. This is in contradiction with the view that dehydration of alcohols takes place at the acid centers on the surface. The energy of activation of the reaction has been obtained. A definite relation between the electrical properties of the bronze and their activity towards IPA dehydration has been observed.

INTRODUCTION

Numerous attempts have been made to correlate the catalytic activity of the transition metal oxides with their semiconducting properties. These results have recently been reviewed (1). Most of the work, however, appears to be on ZnO and NiO and not much has been reported on the important oxidation catalyst V_2O_5 from this point of view.

Vanadium bronzes have been drawing the attention of the solid state chemists and physicists. It has been observed that V_2O_5 with alkali metals can form a series of phases of the composition $M_xV_2O_5$. V_2O_5 is orthorhombic and this structure (α -phase) is retained for $Na_xV_2O_5$ upto $x = 0.02$ (2, 3) and the structure can tolerate a still higher percentage of lithium. In the range $0.22 \leq x \leq 0.4$, the monoclinic β -phase is formed (4, 5). At higher values of x , a new α' -phase structurally similar to the α -phase appears (6). It will be interesting to examine how the changes in structure and electrical properties affect the catalytic activity of the bronzes. The results obtained

for the α -phase range of the lithium vanadium bronzes are reported here.

EXPERIMENTAL METHODS

The preparation of the lithium vanadium bronzes by heating mixtures of V_2O_5 and Li_2CO_3 in the pelletized form and their characterization along with the details of the measurement of electrical conductivity (σ) and Seebeck coefficient (α) have been reported elsewhere (7). Only AR grade chemicals were used.

Surface area of the powdered samples, obtained by the BET method using nitrogen adsorption, were found to be ~ 3 m²/g.

Catalytic decomposition of isopropyl alcohol (IPA) has been studied in a flow reactor using 1 g of the catalysts. A steady supply of the reactant was maintained by an arrangement described by Griffith *et al.* (8). Before each run, the catalyst was activated by passing air at 400°C for 4 hr. Products were collected after allowing about 10 min for the steady state to attain.

The liquid products (IPA, water, diisopropyl ether and acetone) were analyzed

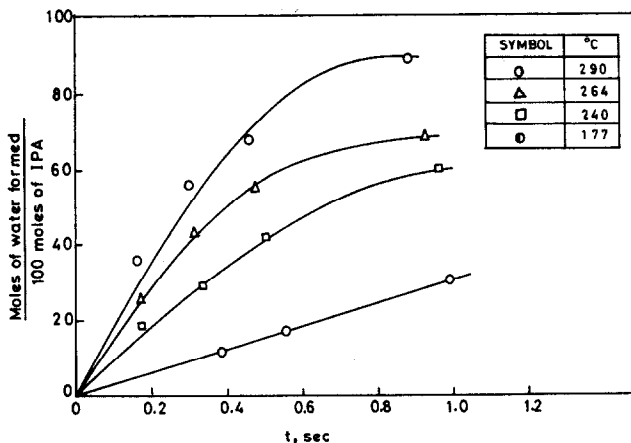


Fig. 1. Conversion vs contact time plots for IPA dehydration on V_2O_5 .

by vapor phase chromatography on an AIMIL Mark II dual column chromatograph using carbowax 20M chromosorb column employing TCD detector and hydrogen carrier gas.

RESULTS AND DISCUSSIONS

The predominant reaction on all the catalysts is dehydration giving water and propylene: more than 97% of the reacted IPA was found to undergo dehydration to propylene. Traces of diisopropyl ether (DIE) have been detected in the products by carrying out the reaction at lower temperatures.

Moles of water formed per 100 moles of IPA fed vs contact time plots are presented in Figs. 1-3 for the different catalysts. The plots (in which the experimental points are shown) were obtained after least square corrections. The initial rates (R) were evaluated from the slope at the origin. Figure 4 shows the Arrhenius plots from which the apparent activation energy of the reaction was calculated.

The results of IPA dehydration are presented in Table 1.

The electrical properties of the vanadium bronzes have been reported elsewhere (7, 9). These can be summarized as follows. The lithium atoms enter into the V_2O_5 lattice interstitially, giving up its electron to the host lattice:

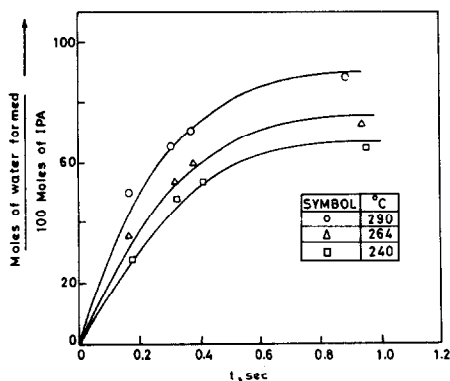
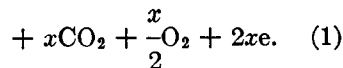


Fig. 2. Conversion vs contact time plots for IPA dehydration on $Li_{0.006}V_2O_5$.

These electrons are trapped, possibly, at oxygen defects. Thermal energy excites the electrons from the trapping centers forming V^{4+} sites. The conduction then arises due to hopping of the electrons from V^{4+} to V^{3+} sites. This hopping model is widely accepted for transport mechanism in the vanadium bronzes (6, 7, 9-11).

With increased doping, the number of V^{4+} centers will increase thus increasing conductivity.

Catalytic dehydration of the alcohols is believed to occur through a mechanism involving the acid centers on the surface of the catalyst. Several workers (12-14) have shown that the dehydration of the alcohols on alumina catalysts decreased by adsorbed sodium and potassium ions. This is attributed to a decrease in the number of the acid centers. Although an electronic mechanism involving the electrical properties of the semiconducting solids is generally postulated for alcohol dehydrogenation (15), the dehydrating activity is generally explained as due to the presence of protonic or Lewis acid centers (16).

Addition of alkali metals as dopants should destroy the acid centers and hence should reduce the catalytic activity. Our experimental results (Table 1) show just the opposite. This shows that the involvement of acid centers cannot successfully explain the dehydration of alcohols on these semiconducting oxides.

Electrical properties of the semiconductors, however, will experience different changes on doping with alkali metals depending upon the type of the semiconductors and also whether they enter into the lattice interstitially or substitutionally.

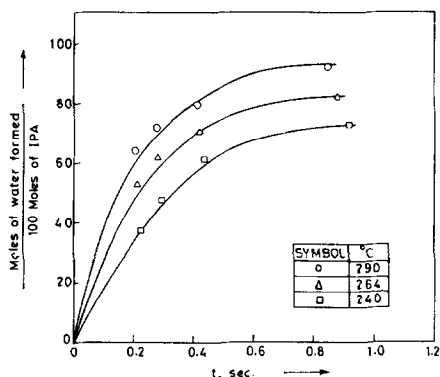


Fig. 3. Conversion vs contact time plots for IPA dehydration on $Li_{0.06}V_2O_5$.

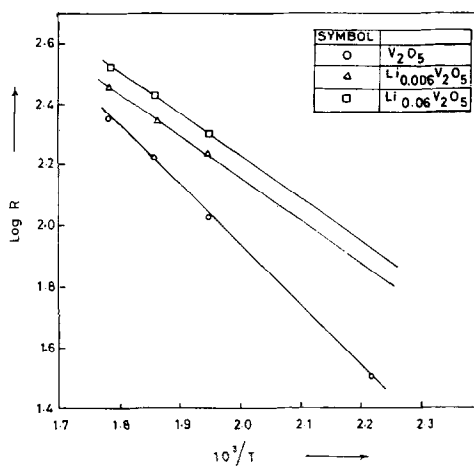


Fig. 4. Arrhenius plots for dehydration of IPA on the different catalysts.

In V_2O_5 (n -type semiconductor), the alkali metal atoms enter into the lattice interstitially increasing its n -type conductivity. The increase in dehydration with the increase in n -type conductivity suggests that dehydration of IPA is an acceptor reaction (17). This is further supported by the results of electrical conductivity measurement of the catalyst pellets under the conditions of the reaction; conductivity was found to increase sharply by introducing IPA vapor.

Similar results have been obtained by Chakrabarty *et al.* (18) on MoO_3 catalysts. It was found that initial doping of MoO_3 with lithium increased n -type conductivity of the catalyst and its dehydration activity. At $x > 0.07$, it became p -type and catalytic dehydration on it was drastically reduced. Keier *et al.* (19) have studied the same reaction on rutile films. By inducing a negative charge on the film by an electric field, work function was found to decrease and catalytic activity to increase. All these results suggest that dehydration of IPA on semiconductors may as well be explained in terms of their electrical properties.

Studying the dehydration of methanol and tertiary butyl alcohol on aluminas and

TABLE 1
Dehydration of Isopropyl Alcohol under Various Conditions

Catalyst	Surface area (m ² /g)	Temp. (°C)	Initial rate (moles/g)	Moles of water formed/100 moles of IPA fed		<i>E_a</i> (kcal/mole)
				Contact time 0.3 sec	Contact time 0.5 sec	
V ₂ O ₅	3.7	240	0.65 × 10 ²	27.5	41.3	9.0
		264	1.04 × 10 ²	40.8	58	
		290	1.40 × 10 ²	54	75	
Li _{0.006} V ₂ O ₅	1.8	240	1.11 × 10 ²	43.2	60.4	6.3
		264	1.37 × 10 ²	52.1	71.8	
		290	1.79 × 10 ²	66.6	89.6	
Li _{0.06} V ₂ O ₅	1.8	240	1.24 × 10 ²	48.5	67	6.3
		264	1.70 × 10 ²	63.1	84.6	
		290	2.06 × 10 ²	75.2	98.7	

silica-aluminas, Figueras *et al.* (20) showed that the presence of a weak basic site adjacent to an acidic site is conducive to dehydration and this view has been supported by Bakshi and Gavalas (21). Figueras *et al.* (20) assumed surface reaction to be the rate determining step. In the case of the catalysts studied by us, the possibility of an acid-base mechanism with lithium serving as a weak basic site adjacent to an acidic site cannot be straight away ruled out. However, according to the same authors, the presence of a basic site would favor the formation of an alkoxide which would give an ether as the product. We, on the other hand, observed that doping of the catalyst with alkali metals reduces the amount of ether in the product. Besides, doping with sodium leads to still higher activity. We believe that sodium will more easily destroy the acidic sites and hence should reduce the dehydration activity if it was due to acid-base reaction.

It has also been observed that the reaction rates on these bronzes are independent of the partial pressure of IPA and propylene but decrease rapidly by increasing the partial pressure of water vapor. The

rate determining step then can be either the surface reaction or the desorption of water. It is known that water desorption is favored by a surface having high electron concentration. Since dehydration of IPA is favored by an increase of *n*-type conductivity of the catalysts (by doping with the alkali metals), desorption of water seems to be the most likely rate determining step. At least this agrees well with the electronic scheme of the reaction.

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